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Comparative study of γ-hidroxybutiric acid (GHB) and other derivative compounds by spectroelectrochemistry raman (SERS) on platinum surface.

R. Jiménez-Pérez[b], J.M. Sevilla[b], T. Pineda[b], M. Blázquez[b], J. Gonzalez-Rodriguez[*a,1]

a School of Chemistry, College of Science, University of Lincoln, Brayford Pool, Lincoln, LN67TS, UK
b Departamento de Química Física y Termodinámica Aplicada, Universidad de Córdoba, Campus de Rabanales, Ed. Marie Curie, E-14071 Córdoba, España.
1 ISE member

Abstract.

The electrochemical behaviour of gamma-hydroxybutyric acid (GHB), the cyclic lactone derivative (GBL), 1-butanol, butyric acid and succinic acid on a platinum electrode in acidic medium has been studied by means of Raman spectro-electrochemistry using the SERS effect. Only GHB and 1-butanol were found to be electroactive substances that can form the acid product mainly and other species in minor proportion through the electro-catalytic oxidation reaction of alcohol group. The interaction of all these molecules with the platinum and platinum oxides, generated during the electrodic process has been investigated in a wide interval of potentials. Succinic acid was found to play the role of both intermediate (to produce the conjugate derivative) and product in GHB electrocatalytic oxidation. Likewise, the electro-oxidation of 1-butanol produced butyric acid predominantly. The carbon (CH_2) and the ring skeletons presented a predominant interaction with the platinum oxide surface for 1-butanol and GBL, respectively.

Keywords: spectro-electrochemistry; GHB, succinic acid; 1-butanol; electrocatalysis; platinum electrode.

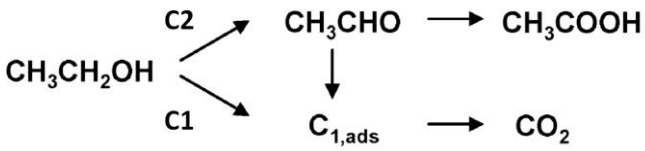
1. Introduction

Gamma-hydroxybutyric acid (GHB) is a substance that can be found naturally in each of the cells of the human body, although it is more abundant in some parts of the body than in others [1,2]. In the brain, the major quantities are in the hypothalamus and in the basal ganglions. Major concentrations also exist in the kidney, heart, skeletal muscle and adipose brown tissue and some considers it to be a neurotransmitter. It can also be present in alcoholic drinks and other food in small quantities. This substance has become infamous by its frequent use as drug in clubs and pubs [3]. The ingestion of this drug in low concentrations (30-100mg/L; 0.28-0.98mM) produces euphoria and lack of inhibition, but if the concentration exceeds 500mg/L (4.9mM) it can produce drowsiness, amnesia, visual hurt, unconsciousness and even death in extreme cases [4].

Recently, a paper on the electro-oxidation of GHB on a polycrystalline platinum electrode by cyclic voltammetry in acidic medium was released [5]. This work is in agreement with the accepted electrochemical behaviour of aliphatic alcohols on platinum electrodes [6-11].

In the last decades, the electro-oxidation of alcohols has received special attention due to its potential use as fuel. The generation of energy using fuel cells has attracted great attention due to the major energetic demands of the present society, the depletion of the fossil fuels, the problem of environmental pollution and the low energetic utilization of the thermal processes associated with the use of fossil fuels. Liquid fuels, especially alcohols, have been evaluated as alternatives for this application. Ethanol has been a major center of attention recently as it is a less harmful substance and more stable than other options, such as methanol. In addition it is easy to store and produce. The electro-oxidation of ethanol has been mainly centered on platinum electrodes on acid media due to the fact that this is considered to be the best monometallic catalyst for the electro-oxidation of small organic molecules. Nevertheless it presents three problems associated to its electrochemical use [11]: (i) for concentrations that would be reasonable in the production of energy the oxidation of ethanol to CO_2 has a minor contribution. The principal route in the mechanism, called C2, produces the conversion of ethanol in acetaldehyde and acetic acid. (ii) The route called C1, for which the ethanol mainly turns into CO_2, is a process with complex steps. This route, in addition, implies the adsorption of CO and CH_x residues. (iii) Finally, the global reaction rate for the electro-oxidation of ethanol on a platinum electrode, despite being the most efficient of these

processes, is considered to be too slow for practical uses. The second problem indicated, tied to the oxidation by the route C1, is the most important. Studies by FTIR (Fourier Transform Infrared Spectroscopy, SERS (Surface-Enhanced Raman Spectroscopy) and DEMS (Differential Electrochemical Mass Spectrometry), between others [12], have verified that the presence of adsorbed carbon monoxide is the principal source of poisoning of the electrode in the oxidation of the alcohols. Both routes of the electrooxidation of the ethanol are shown in scheme 1 [13]



Scheme 1

This type of mechanistic aspects that have been studied in ethanol and other alcohols are of interest to confront the study of the electro-oxidation of the GHB on platinum electrodes and it is considered to be a starting point to find the methodology that makes possible the rapid detection of this hydroxyl acid.

In this context, the present study will employ Surface Enhanced Raman Spectroscopy (SERS) to investigate the electro-oxidation of GHB on a platinum surface in a wide potential interval. For this purpose we analyzed the comparative behavior of four-carbon derivative compounds in the same experimental conditions: 1-butanol, gamma-hydroxy butyric lactone (GBL), butyric acid and succinic acid. Although SERS has extremely high surface sensitivity and has been applied in surface electrochemistry of Ag, Au and Cu surfaces, the sensitivity is low for the Pt group. However, the advantages of SERS for the eletrooxidation studies on this important catalyst outweigh the disadvantages. In this sense, SERS has two main advantages. First, SERS is based on visible light rather than infrared light, allowing the detection of vibration modes below 700 cm^{-1}, a region that is difficult to access with infrared spectroscopy due to the limited transparency of most optical windows in this range. However it is still of interest as most metal-adsorbate vibrations lie in this region. Second, water molecules ubiquitous in most electrochemical systems have a small Raman scattering cross-section facilitating the collection and interpretation of spectra. This is particularly interesting to observe the co-adsorption processes of intermediates, water and other components present in the electrolyte. To the best of our knowledge, our analysis of the Raman

spectroscopic detection of the adsorbed intermediates and reaction products generated in the dissociation and electro-oxidation of GHB and their derivatives by SERS has not yet been reported in the literature.

2. Material and methods

Gamma-hydroxy butyric lactone (GBL) was obtained from Aldrich (reagent, minimum 99% purity). 1-Butanol (≥99% purity), butyric acid (≥99% purity) and succinic acid (≥99% purity) were purchased from Sigma-Aldrich. Sulphuric acid (98% purity) and phosphoric acid (85% purity) were purchased from Merck. Semiconductor grade sodium hydroxide was purchased from Sigma-Aldrich. All solutions were prepared with deionized water produced by a Millipore system (Millipore, Maryland, US). GHB sodium salt, was prepared and identified as is described in reference 5.

Cyclic Voltammetry (CV) and chronoamperometry analyses were performed with an Autolab (PGSTAT 302N) instrument attached to a PC with NOVA software for the control of the experiments and data acquisition.

The electrochemical setup for the oxidation of GHB consisted in a three electrode system DropSens Screen-Printed Carbon Electrode (SPCE) with previous deposition of Pt on the graphite working electrode (K_2PtCl_6 Sigma-Aldrich, ACS reagent).The reference electrode and counter electrode were made of silver and platinum, respectively. To obtain the electrodeposited Pt surface onto the SPCE, the following procedure was employed. The SPCE was immersed into 50 mL of platinum solution (K_2PtCl_6) 0.2% containing 0.01 mol L^{-1} KCl as the supporting electrolyte. After that, a constant potential of -0.4 V (vs. Ag–SPCE) was applied for 300 s. The procedure was repeated three times. The electroactive surface area was determined using the hydrogen adsorption/desorption voltammetric peaks of platinum electrode with a known charge density of 210 μC/cm^2 in 1.0 M H_2SO_4. A value of 4.18±0.12 cm^2 was found and used for normalise the current intensity in the cyclic voltammograms presented in this work. The open circuit potential of the cell, OCP, was measured in the presence of GHB for the platinum surface electrode newly cleaned. The obtained value was 0.178±0.012 V and was found in the first minute of the OCP-t curve registered. All the measurements realized in this work were carried out with freshly and deoxygenated (pure nitrogen for 20 min) prepared solutions.

Surface Enhanced Raman Spectroscopic (SERS) measurements were performed with a HORIBA Jobin Yvon LabRaman spectrograph with a holographic grating of 600 grmm^{-1}. The excitation line was provided by a 17 mW He-Ne laser at 633.0 nm. The laser beam was focused through an Olympus 50x long working distance objective (0.5 NA) into a 2μm spot at the electrode surface. Signal averaging of two spectra with spectrometer resolution better than 3 cm^{-1}, 60 s acquisition time each, was performed. The same setup was used for the spectro-electrochemical measurement and consisted in a three electrode system DropSens (Pt-SPE). A volume of 40 μL was placed on the Pt-SPE surface for each experiment, covering completely the three electrodes of the Pt-SPE. A microscope glass cover slip (Fisher scientific coverslips) was placed over the sample drop to perform each experiment in order to avoid the oxygenation of the sample.

The potential was held constant for the necessary time until the stationary current of the j-t curve was reached. In all cases the stationary current observed is consistent with a catalytic mechanism for the electro-oxidation reaction of GHB and derivatives. Under the experimental conditions used in this work, stationary currents are obtained in a time interval of around 100-120 seconds with independence of the surface state and the concentration of the electroactive substance. This procedure allowed us to ensure that the adsorbed GHB and their fragments are present on the electrode surface at the start of each SERS experiment. The laser beam was focused on one of the Pt agglomerates at the electrode surface. An AFM image of the platinum surface obtained as a result of the surface conditioning is shown in Figure 1. This image was obtained using a Bioscope Catalyst AFM (Bruker) coupled to a laser Nikon Eclipse TE2000-S. The experiment was performed by using Peak Force Tapping, employing Bruker ScanAsyst Air tips with a spring constant of 0.4 N/m and a resonance frequency of 70 KHz. The theoretical lateral resolution is 12nm. The figure shows a typical image of the platinum surface after electrodeposition on carbon electrode. Several clusters/agglomerations are observed and their formation depends on the time and applied potential. This visualization provides information of the surface regions where we can focus the laser in the Raman experiments.

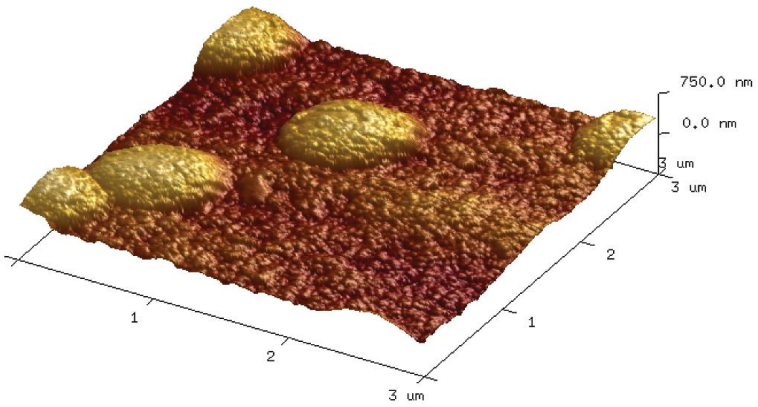


Figure 1. AFM image of the platinum surface by electrodeposition on Screen-Printed Carbon Electrode (SPCE) on an area of 3x3 μm^2 (256x256 px) with a scan rate of 0.5 Hz.

3. Results and discussion

3.1. Cyclic voltammetry

Figure 2 shows the superimposed voltammograms for the set of studied substances. We can observe that GHB and 1-butanol present oxidation peaks in the range studied whereas for the other compounds only some type of interaction is observed. This is revealed by the partial perturbation of the UPD peaks for hydrogen at low potentials as well as by the delay on the platinum surface oxidation, with the corresponding decrease of the reduction peak of the platinum oxides at 0.45 V.

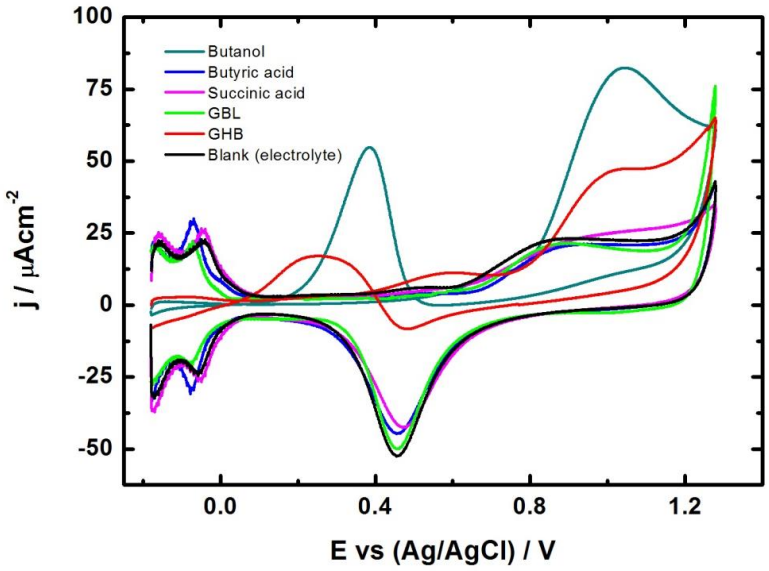


Figure 2. Cyclic voltammograms of the compounds registered on a platinum film deposited on a carbon electrode. Test solution: 0.5 M GHB + 0.5 M phosphoric acid.

The current density of 1-butanol and GHB is corrected by a factor of 10 and 3, respectively. Scan rate: 20 mV/s

3.2. In Situ Surface Enhanced Raman Scattering (SERS) Spectro-Electrochemistry of GHB

Figure 3 shows a series of SERS spectra collected for the platinum electrode in a 0.5 M GHB + 0.5 M phosphoric acid solution at several potentials. As explained in the experimental section, the spectrum was registered after applying the potential during the necessary time to reach the stationary condition (stationary density current in a j-t curve). This procedure allowed us to ensure that the adsorbed GHB and their fragments are present on the electrode surface at the start of each SERS experiment.

With the exception of the bands corresponding to the adsorbed phosphoric acid at 367 cm^{-1} and 770 cm^{-1}, also observed in the blank electrolyte spectrum, the bands in these spectra correspond to GHB and water adsorbed species being formed/consumed in the potential dependent adsorption processes.

Very weak bands at 520 cm^{-1} and 1935 cm^{-1} can be observed and associated to the bridge CO, although a contribution of lineal CO that diminishes up to disappearing cannot be categorically rejected either [12,14,15]. A similar behavior with the potential is found for 1-butanol in the region 1650-2250 cm^{-1} as described in the following section. The CH stretching mode at 2841 cm^{-1} [16], and the OH stretching of the adsorbed water at 3149 and 3320 cm^{-1} (not shown in spectra of figure 3) [17] are also present. On the other hand a peak at 950 cm^{-1} is assigned to the symmetric stretching of C-C bond [14]. Also, at 830 cm^{-1}, a band overlapping with that corresponding to the phosphate electrolyte is assigned to the deformation scissoring mode of the carboxylic group [18]. The intensity of these two bands changes with the potential of inverse form what is compatible with a different interaction of these groups with the free and oxidized platinum surface. The weak bands in the range between 1000 and 1400 cm^{-1} present an important overlapping and correspond to the adsorption stretching band of C-OH, the bending bands of groups CH_2 and OH, and the symmetric stretching of OCO group [14].

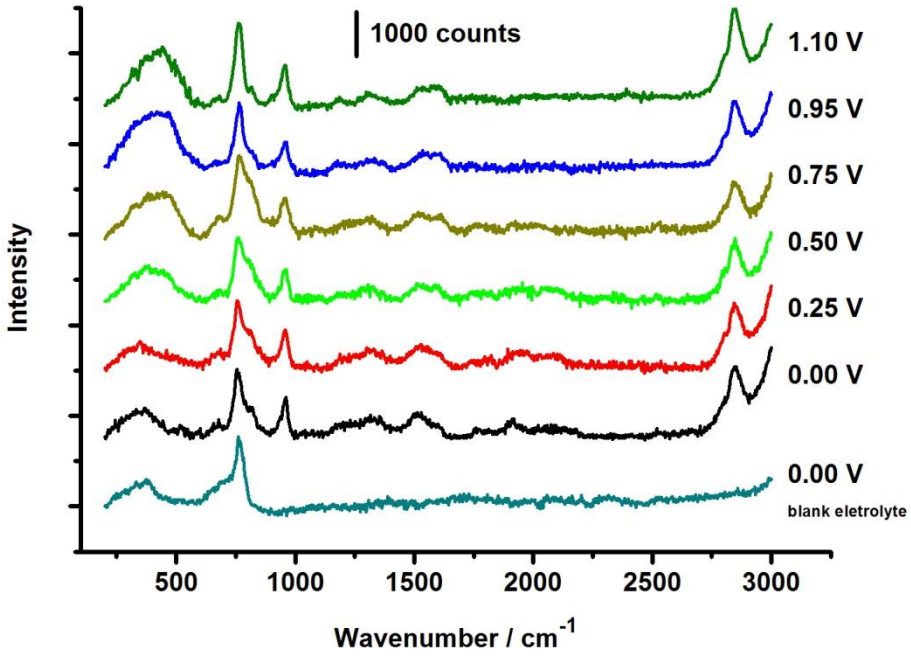


Figure 3. SERS spectrum collected with a platinum surface electrodeposited on carbon electrode. Applied potential vs Ag/AgCl is shown in the figure. Test solution: 0.5 M GHB + 0.5 M phosphoric acid. The spectra collected with an acquisition time of 60 s were averaged and corrected by subtraction of a baseline.

It is necessary to emphasize the presence of CO adsorbed despite the known fact that in phosphoric media the formation of CO_{ads} from dissociative oxidation of alcohols and their further oxidation is strongly inhibited [11]. On the other hand, the presence of the bands associated with interfacial water molecules can relate to the catalytic role of the solvent in the electro-oxidation of GHB on Pt electrodes. Also, we call the attention on the appearance of weak bands in the zone 1500-1600 cm^{-1} for all the potentials where the presence of the GHB or an intermediate adsorbed on platinum surface can be recognised by a weak peak at 1510 cm^{-1} corresponding to the fingerprint chain vibration (bending of $–CH_2$- and other group) [19]. In the same way, when the potential increases, we observe that a peak is visible at 1590 cm^{-1} (only as a shoulder below 0.5 V) corresponding to asymmetric stretching mode of the carboxylic group and one that corresponds with the selective conjugated C=C stretching mode [18,20,21]. This support the possible formation of the conjugate compound (probably maleic acid), together with the succinic acid, on platinum surfaces as reaction products under the experimental conditions studied. Finally, very weak signals at 1740-1770 cm^{-1} that

diminish until disappearing in the zone for carbonylic groups associated to aldehyde intermediates can be observed [22].

Inspection of the potential dependence of the spectra in the zone of low wavenumbers showed an evolution of the band at 370 cm^{-1} corresponding to the interaction of phosphoric electrolyte with platinum surface at potentials lower than 0.0 V, as indicated above. A band at 430-470 cm^{-1} started gradually appearing at 0.5 V, most likely from the Pt-OH and Pt-Ox vibrations [23,24]. The increasing intensity of this last band in a parallel way to the formation of Pt oxides and hydroxides on the surface of the electrode is in good agreement with the observed peaks in the voltammogram of the blank electrolyte and that supports the catalytic role of the surface oxygenation in the electro-oxidation reaction of GHB.

The behaviour in this last region is common for all the spectra of the studied compounds.

3.3. In situ SERS of 1-butanol.

1-butanol is the other electroactive substance on platinum electrode shown in section 3.1. Good resolution bands in the zone 1000-1400 cm^{-1} (Figure 4) with bands at 1035, 1184, 1250, 1285 and 1336 cm^{-1} assigned to δ(P-OH), ν(P=O), δ(CH_2), δ(OH) and δ(CH_3), respectively can be observed. Table 1 summarises the responses obtained for GHB and different GHB derivatives studied indicating band presence and trend when the potential used is increased from 0 to 1.1 V.

In the case of 1-butanol, the intensity of the first two bands diminishes when the potential increases until they practically disappear, which indicates that the interaction with phosphoric acid diminishes strongly with the formation of oxygenated forms of platinum.

Table 1. SERS bands in the region 1000-1400 cm^{-1} for GHB derivative compounds and the trend of peak intensity with increased potential*

$\bar{\nu}/cm^{-1}$	**1-buthanol**		**butyric a.**		**succinic a.**		**GBL**	
/assignation	peak	trend	peak	Trend	peak	trend	peak	trend
1015 / δ(P-OH)	√	↓↓	√	↓↓	√	↓↓↓	—	—
1122 / δ(ring)	—	—	—	—	—	—	√	↑
1184 / ν(PO)	√	↓↓	√	↓↓	—	—	√	↓↓↓
1250 / δ(CH_2)	√	↑	√	↓	√	↓	√	=
1285 / δ(OH)	√	↑↓	√	↓	√	↓	√	↑
1336 / δ(CH_3)	√	↓	√	=	—	—	—	—

(*) In this zone, GHB shows a great overlapping of bands that difficult the assignation (see Figure 3).

In contrast, the bands at 1250 and 1285 cm^{-1} increase indicating the adsorption of 1-butanol. These results suggest the co-adsorption of electrolyte and 1-butanol only at low potentials. A small decrease of this last band and that corresponding to $\delta(CH_3)$ at high potential are related with the oxidation process. In this sense, in the zone 1400-1650 cm^{-1} in figure 4, a band at 1590 cm^{-1} (as shoulder) that increases with potential can be observed corresponding to the formation of the butyric acid as reaction product of the oxidation of 1-butanol. This band is an indicator of the strong interaction of carboxylic group with the platinum surface.

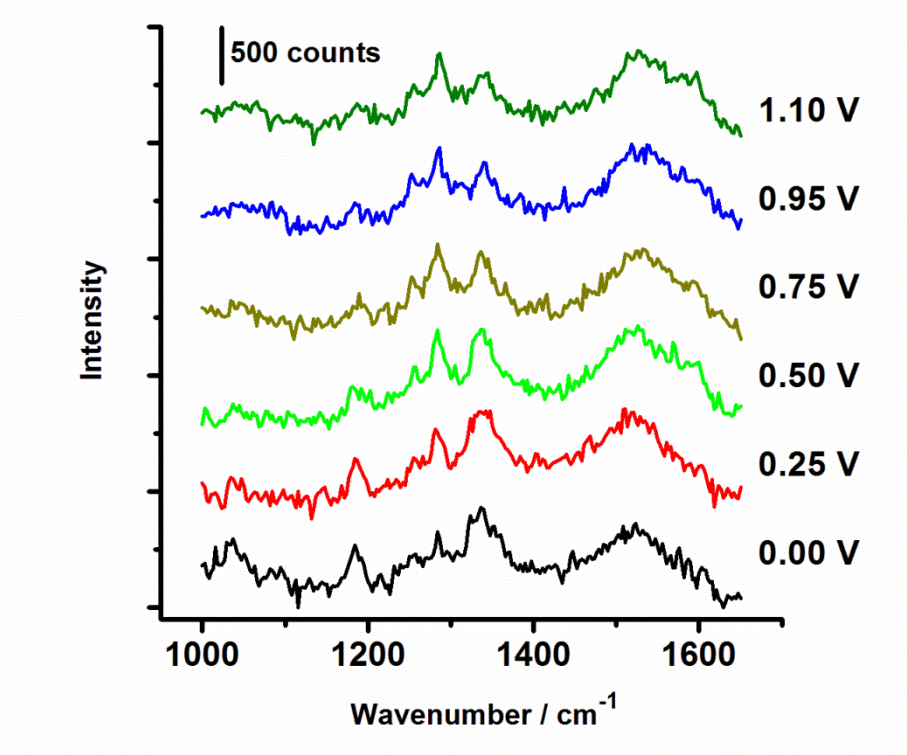


Figure 4. SERS spectra (zone 1000-1650 cm^{-1}) of 1-butanol with a platinum surface electrodeposited on carbon electrode. Test solution: 0.5 M solute compound + 0.1 M phosphoric acid. Two spectra collected with an acquisition time of 120 s were averaged

In figure 5, some very weak bands are also observed at 1750, 1930 and 2050 cm^{-1} that disappear with increasing potentials and indicate the presence of a derivative aldehyde and of bridge and atop forms of carbon monoxide, respectively.

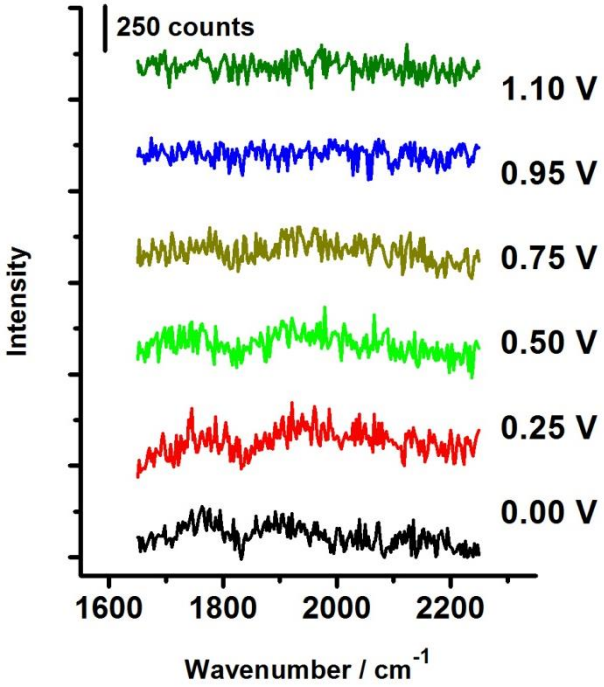


Figure 5. SERS spectra (zone 1650-2250 cm^{-1}) of 1-butanol with a platinum surface electrodeposited on carbon electrode. Test solution: 0.5 M solute compound + 0.1 M phosphoric acid. Two spectra collected with an acquisition time of 120 s were averaged.

Finally, it is necessary to emphasize the four bands observed in figure 6 in the zone 2850-2950 cm^{-1} corresponding to symmetric and anti-symmetric stretching modes of the CH_2 and CH_3 groups of 1-butanol and the derivatives resulting of the electro-oxidation reaction. For these bands a decrease associated with a difference in the strength of adsorption, as the potential increases, and the competition with the adsorption of the main product of reaction, butyric acid, can be observed.

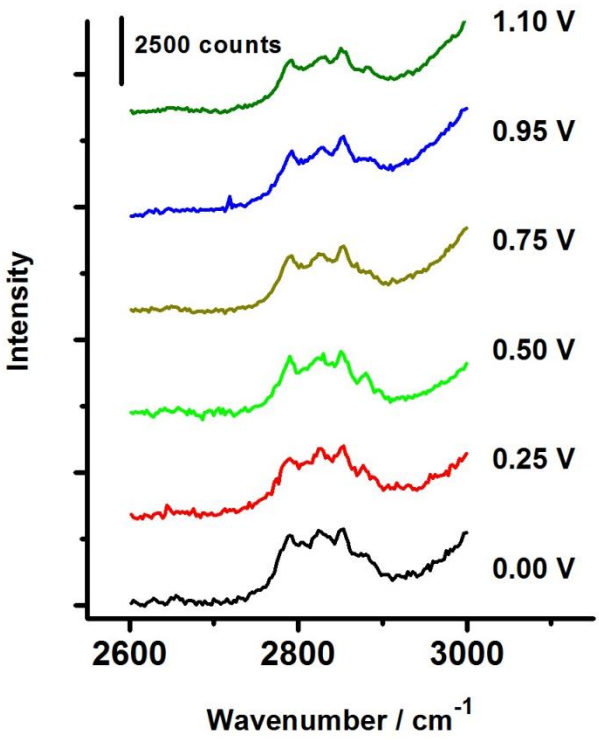


Figure 6. SERS spectra (zone 1650-2250 cm^{-1}) of 1-butanol with a platinum surface electrodeposited on carbon electrode. Test solution: 0.5 M solute compound + 0.1 M phosphoric acid. Two spectra collected with an acquisition time of 120 s were averaged.

3.3. In situ SERS of butyric acid, succinic acid and GBL.

In relation to the complete spectrum for each one of these substances it is necessary to highlight the bands observed for butyric and succinic acids in the zone 1000-1400 cm^{-1} (Table 1) agree with the molecule structure. This way, for succinic acid we observe only the band at 1253 and 1284 cm^{-1} assigned to $\delta(CH_2)$ and $\delta(OH)$, respectively. In the case of butyric acid a peak at 1335 cm^{-1} corresponding to $\delta(CH_3)$ is also observed. It is worth noting that the peaks corresponding to the phosphoric acid interaction in this zone present a very low intensity. On the other hand, the spectrum of the lactone (GBL) shows the same bands that succinic acid in this zone (Table 1) together with a singular peak at 1122 cm^{-1} that can be assigned to the vibration of the carbon chain in the lactone ring [25]. This band increases their intensity with the potential indicating that the interaction is stronger with surface platinum oxides. In this sense, only a very weak band corresponding to the phosphoric acid at 1184 cm^{-1} can be observed.

The spectra of butyric acid and succinic acids in the zone 1400-1700 cm^{-1} are independent from the applied potential and, in both cases, the bands at 1600 cm^{-1} stand

out (figure 7). The higher intensity found for succinic acid suggests a strong interaction of the carboxylic groups of the molecule with the platinum surface. In relation with the strong adsorption of succinic acid on Pt, there are also evidences of it in the voltammograms of figure 2 where the current intensity of the reduction peak of oxides diminishes close to 20 % in comparison with the current intensity of the blank electrolyte. It is also worth noting that a small decrease of this band when the potential increases indicates some weakening of this interaction with the presence of metallic oxides.

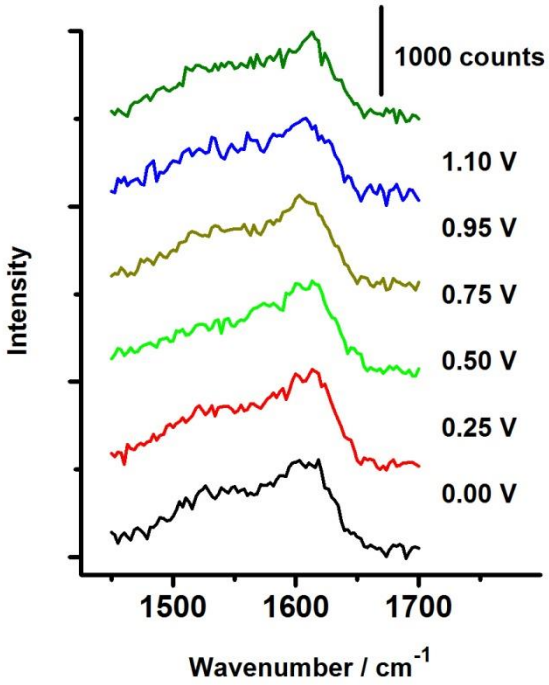


Figure 7. SERS spectra (zone 1400-1700 cm^{-1}) of the succinic acid with a platinum surface electrodeposited on carbon electrode. Test solution: 0.5 M solute compound + 0.1 M phosphoric acid. Two spectra collected with an acquisition time of 120 s were averaged.

The bands observed at 1590-1600 cm^{-1} for the acid derivatives support the theory of an electro-catalytic formation of succinic acid from GHB as can be seen by the evolution of these bands at this wavenumber in the spectra shown in figure 3. Having said this, the possible formation of dienic derivative compounds (maleic acid, probably) cannot be rejected, as the vibration at this wavenumber can also be assigned to the stretching of the C=C in this family of compounds [18].

Figure 8 shows the spectra of GBL in the zone with the presence of a band at 1650 cm^{-1} that can be assigned to the stretching of CO groups in the cyclic compound [25]. The

increase of band intensity with the potential suggests a major interaction of the lactone in the zone of platinum oxides according to the results obtained in the range 1000-1200 cm^{-1} where we can see that the peak intensity for the band at 1122 cm^{-1} also increases (figure 8).

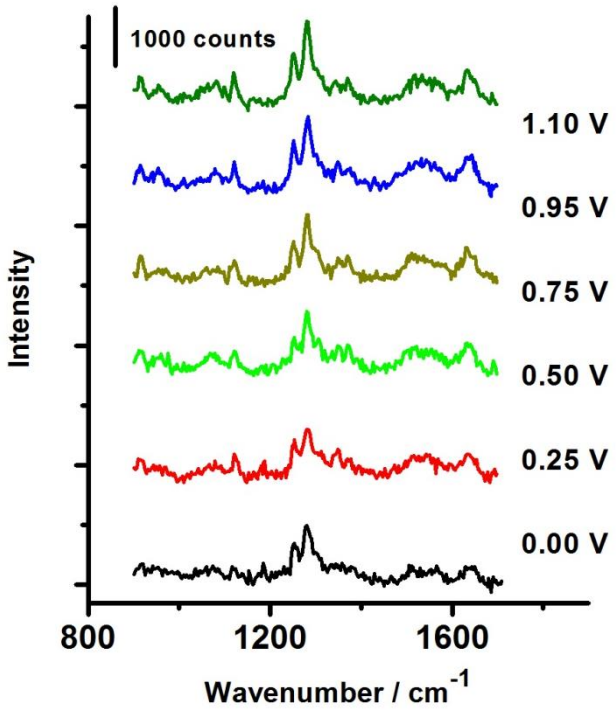


Figure 8. SERS spectra (zone 900-1700 cm^{-1}) of the GBL with a platinum surface electrodeposited on carbon electrode Test solution: 0.5 M solute compound + 0.1 M phosphoric acid. Two spectra collected with an acquisition time of 120 s were averaged.

The set of the results obtained do support the hypothesis of a higher electrochemical activity of 1-butanol and GHB compounds in this region. In particular, in the case of the electro-oxidation of GHB, we can highlight the selective apparition of the peak at 1590 cm^{-1} corresponding to the formation of succinic acid as the principal reaction product.

These results are also in agreement with the general scheme accepted (Scheme 1 for ethanol) for the catalytic electro-oxidation of alcohols on platinum [12]. In this sense, GHB follows the way C2 as principal route as it is deduced of the results showed in this work.

In particular, the results by using in situ Raman spectroscopy suggest that the oxidation of GHB occurs on specific sites on the catalytic surface of platinum with the participation of co-adsorbed water molecules or the same one as hydroxide platinum species, following the scheme:

$Pt + H_2O = PtOH$ (or $PtOH_2$)

$Pt + GHB = PtGHB_{ads}$

$PtOH + PtGHB_{ads} = 2Pt + GHB_{OX}$ (succinic acid)

Some authors have suggested that the oxidation of alcohols occurs in different stages according to a mechanism similar to that suggested by Langmuir-Hinshelwood involving oxygenated species adsorbed on the metallic surface of the electrode close to alcohol molecules or alcohol intermediates [26]. Our results point at a similar mechanism of reaction for the electro-oxidation of GHB.

4. Conclusions

The interaction of gamma-hydroxybutyric acid (GHB), the cyclic lactone derivative (GBL), 1-butanol and butyric and succinic acids on a polycrystalline platinum electrode in acidic medium has been studied by means of spectro-electrochemistry Surface Enhanced Raman Spectroscopy (SERS) in a wide interval of potentials. GHB and 1-butanol are the only electroactive substances as is demonstrated by cyclic voltammetry, although some interaction on platinum surface is observed for all the molecules by in-situ SERS.

In the experimental conditions developed for this work, the spectro-electrochemical results demonstrated that succinic acid plays the role of both intermediate (to produce the conjugate derivative) and product in the GHB electrocatalytic oxidation reaction of the alcohol group. Likewise, the electro-oxidation of 1-butanol produced butyric acid predominantly.

For each compound studied, co-adsorption with the solvent and the electrolyte is shown, particularly at low potential. Also, the carbon (CH_2) and the ring skeletons presented a predominant interaction with the platinum oxide surface for 1-butanol and GBL, respectively.

In this work, we report for the first time the Raman spectro-electrochemical detection of the adsorbed intermediates and final products in the dissociation and electro-oxidation of GHB and some derivatives compounds. This comparative study can be crucially important to find a methodology that makes possible the detection of GHB of a rapid form. It also worth remarking the difficulty of achieving Raman signals for these

substances to follow the electrochemical interactions with platinum surfaces and with platinum oxides formed during the electrodic process. It is well known that Raman is a very weak process and the sensitivity of the technique is not high. Just a monolayer of target substances were deposited on the Pt electrode and only through the SERS effect has been possible to achieve the required sensitivity to follow these interactions. This study can serve the purpose of informing future Raman spectro-electrochemical investigations of organic compounds and their interactions with SERS active substrates, such as platinum and their oxides.

5. Acknowledgments

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